EXTRACTION OF POTASH ALUM FROM ALUNITE

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THE EXTRACTION OF POTASH ALUM FROM ALUNITE

A THESIS

PRESENTED BY

N. C. FISCHER AND M. M. WILSON

TO THE

PRESIDENT AND FACULTY

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THE AUTHORS WISH TO EXPRESS THEIR GRATITUDE TO PROFESSOR MC CORMACK FOR GUIDANCE AND ASSISTANCE GIVEN IN THIS WORK.

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OBJECT.

The object of this work was to study the conditions and determine which conditions are the best for the extraction of potash alum from alunite. If such process, using the conditions thus determined, is employed, the extraction of the alum will be more economical than methods heretofore used, most of which require a sulphuric acid leaching solution and generally require a source of potash other than the alunite itself.

At present the sources of potash salts seem to be growing smaller in number so that any new source of potash or potash alum is very valuable.

Alunite, containing as it does the elements of potash, aluminum and the sulphate radical, is a source not only of potash salts, but of potash alum, the value of which can be understood from a review of its varied industrial

uses. Probably the three greatest uses of potash alum are in the dyeing industry where it is used as a mordant; in the tanning industry where it is used in place of a tanning agent in the preparation of light skins; and in the paper industry where it is used in connection with some substance such as rosin or casein as a sizing agent. Alum is also used extensively in preparing non-flammable cloth and wood, in water proofing cloth by the formation of an alum soap or gelatin precipitate, and in medicine, butter coloring and so forth.

With these large markets for alum open, it is evident that a method for the extraction of alum from the relatively cheap alunite is worth while commercially.

HISTORY OF THE PROCESS.

So far the alum manufactured in this country previous to the war was made from domestic alumina and imported potash. Deposits of alunite have now been found in Utah and these deposits can profitably be used as a source of alum.

The history of the process of manufacturing potash alum from alunite in foreign countries has been reviewed in Bulletin 620-K issued by the U.S.G.S. The facts given in this bulletin are given in the following.

In Sicily the alunite is made into heaps and calcined in the open air. At Tolfa. where the manufacture is carried out on a larger scale, the material is roasted in furnaces like lime kilns. The material is heated in large pieces by the flame without direct contact with the fuel until sulphur dioxide begins to escape. The calcination requires

about three hours, the mass losing about thirty-five percent in weight. During the ignition the excess of alumina beyond that necessary to produce alum is rendered insoluble and no longer has the property of precipitating basic sulphate from solution. The calcined mass is exposed to the air on a clay floor for some weeks during which time it is occasionally moistened. The mudlike product is agitated in boilers at seventy degrees centigrade and the clear decanted liquid of density ten to twelve degrees Baume is evaporated to thirty-two degrees Baume and crystallized in small wooden tubs. Any iron present is insoluble and may be separated by recrystallization. In this way "Roman Alum" was largely produced.

At present the treatment of alunite with sulphuric acid and potassium sulphate is largely used in preparing alum. Several methods of procedure have been recommended for this process.

On the ignition of alunite the free alumina is first rendered anhydrous and soluble in sulphuric acid. At a higher temperature the basis sulphates become soluble, but if the temperature rises too high, the alumina becomes vitrified and insoluble. Ignition for three hours at eight hundred degrees centigrade has been recommended as the best means of rendering the maximum of both these substances soluble. The composition of the calcined mass is determined and sulphuric acid is used in proportion to the amount of soluble sulphate present. For a product of the following composition:

Potassium sulphate - - - - - -14%
Aluminum sulphate (as alum) -.55%
Ferric oxide - - - - - - - - .8 %
Free aluminum sulphate - -- -18½%
Siliceous residue - - - - - -21-60/100%.

the following proportions would be most satisfactory. Into a clay oven is poured twelve and a half tons of sulphuric acid of fifty-two degrees Baume diluted to thirty-two degrees

Baume and heated to eighty or ninety degrees centigrade. Eight tons of the calcined material is then added in portions and well stirred. After the whole has been added, the liquid is left for two hours and then evaporated to thirty-eight degrees Baume and treated with two and seven tenthstons of potassium sulphate. The process up to this point occupies about ten hours. After a further period of thirteen hours the clear liquid is decanted off, its density should not exceed forty-two degrees Baume. The muddy liquid remaining is reduced to twenty four degrees Baume by the addition of mother liquor from a previous crystallization, stirred, allowed to settle, drawn off clear, mixed with the first decantate, and crystallized in a vat. After one day the crystals are removed, dissolved and recrystallized. The muddy residue is crystallized out for a further crop of alum. The total yield of alum is about two and one third times the origin-

al weight of ore. The insoluble matter contains three percent alumina and two and one one hundredth percent potassium sulphate in addition to silica and so forth.

According to another investigator the best temperature for the roasting is five hundred degrees centigrade and the acid used should have a density between 1.297 and 1.530.

An outline of the process of extracting alum from alunite at the Australian deposit of Bulladelah is as follows: the mineral is ground and then calcined in reverbratory furnaces to dehydrate and drive off part of the sulphur trioxide. It is next treated with a weak solution of sulphuric acid in lead lined tanks heated to boiling by steam jets. The liquor is allowed to settle in the same vats and the clear solution is run into crystallizing tanks which are kept in constant agitation while cooling. Here the alum crystallizes out while the aluminum sulphate remains in so-

lution. The residue in the vat is boiled again with water and the solution run off again in the same way. The liquor containtin aluminum sulphate is then returned to vats and sufficient of the calcined material added to completely neutralize any free acid. It is heated to the boiling point and ebullition continued until partial reversion takes place. The reversion is accompanied by a precipitation of the hydrated ferric oxide.

The alum after collection is washed and then refined in vats similar to. but deeper than those originally employed, and the concentrated solution is run into roaching tuns in which it is crystallized. It is then broken up and packed ready for shipment.

The aluminum sulphate, after all the alum has been crystallized from it, is concentrated in small vats heated by steam coils and the poorer grades of aluminum sulphate are formed by running the liquor onto lead tables and break-

ing the solidified material into blocks. Better grades, containing over seventeen percent soluble alumina, are cast on copper trays. These slabs vary in color from yellow to green but after grinding they become snow white.

It is possible by the addition of potassium sulphate, to convert all of the alumina contained in the rock into alum if desired, but the most profitable method of treatment when the better grades of aluminum sulphate can be sold at standard prices, is to make only as much alum as there is sulphate of potash present to produce, and convert the rest of the alumina into soluble sulphate of alumina.

By this process the stone yields about eighty percent of alum. According to the statistics for the mining industry of New South Wales, the output of alum for the years 1856 to 1908 was valued at $450,000.00 and for the years from 1908 to the end of 1913, at $190,000. Since 1908 about one thousand

two hundred tons of the rock have been taken out annually and shipped to England where the alum could be extracted with much less expense than was possible in Australia.

The analysis of alunite is evidently not a constant thing in all localities as most authorities give varying results. However, "Mineral Resources" for 1915 gives a definite formula for alunite as $K_2O.3Al_2.O_3.3SO_3.6H_2O$. In their book, "Chemistry of Manufacturing Processes", Bertram Blount and A. G. Bloxam give an analysis as follows:

SiO_2 - - - - - - -13.4 ✓
Al_2O_3 - - - - - - 35.5 ✓
Fe_2O_3 - - - - - - .05 ✓
K_2O - - - - - - - 12.5 ✓
SO_3 - - - - - - - 30.0 ✓
H_2O - - - - - - - 8.5 ✓

Their description of the process of manufacture is evidently based on the Italian process, as they describe a roasting at 500° centigrade.

They state, however, that if water and no acid is used in leaching the material, the alum crystallizing out, is a basic double sulphate of the formula $K_2O.SO_3.Al_2O_3 2SO_3$. Unlike the ordinary alum this material has a neutral reaction instead of the usual acid reaction of alum and it crystallizes in cubes instead of in the usual form. When sulphuric acid is used as the leaching agent, the usual alum crystallizes out. The neutral alum, however, is valuable for certain purposes.

The literature on the subject of preparing alum from alunite is practically limited to what has been given here. The majority of books on industrial chemistry describe the process in use at Tolfa, Italy.

EXPERIMENTAL WORK.

To investigate the conditions to which the alunite should be roasted, the following method was decided upon. The small amount of literature that was available on the subject described roasting at anywhere from 500° centigrade to 800° centigrade. In order to come well within these limits, it was decided to make runs between 400° C. and 900° C. inclusive. To eliminate any influence which a strong oxidizing or reducing atmosphere would have upon the roasting of the alunite, the electric muffle was chosen. Another factor in its favor was the ease with which temperatures could be maintained at a constant value.

From preliminary runs made on a sample of ground alunite, it was found that when heated for two hours at approximately 900° C. no soluble alumina was formed. Upon evaporating the extraction from this run to dryness, a yield of 21.6% extracted matter was obtained. This

was analysed and found to be potassium sulphate. Since our object was to obtain alum, 900° was thus established as being above the upper limit of our temperature range. At 900° C. the sample showed a loss in weight of 28% after one hour of heating. Further heating gave no increase in volitalized matter.

The alunite, as received, was in large lumps. This was first run through a jaw crusher and the crushed material ground in pebble mills until it passed a 150 mesh sieve. This material was thoroughly mixed and bottled. Twenty-five gram samples were weighed from this material and placed in roasting dishes. In the mean time the electric furnace was turned on and brought up to the decided temperature. A number of dishes corresponding to the number of hours the run was to cover, were placed in the furnace and the roasting was started. At the end of each hour one of the dishes was removed and allowed to cool. When

cool the roasted alunite was carefully removed and weighed. The difference between this weight and the original weight gave the loss on ignition. After the last dish had been removed the temperature of the furnace was raised 100° and the entire procedure repeated with fresh samples of alunite.

The roasted alunite samples were extracted with about 300 cc's of hot water. Trouble was at first experienced at this point by the alunite's setting to a hard rock-like mass. This was overcome by stirring the mass for a few minutes with about half as much hot water as had been used at the beginning, followed by settling, filtering, and a second leaching of the precipitate with a small amount of hot water. The combined filtrates from each extraction were evaporated to dryness on the water bath and then heated to 110° for about one hour in the drying oven. This dried material was then scraped out, weighed and ground to

powder in an agate mortar and then placed in weighing bottles. The extracted weight was recorded. From each sample bottle a .5 gram sample was taken for analysis. The samples were then analyzed for alumina and potash. The results of this work are shown in the data sheet.

The data gives the time and temperature of roasting with the percent loss in weight on roasting, the percent of dried extracted material, the percent aluminum sulphate in the extracted matter calculated from the percent of aluminum oxide weighed, the percent of potassium sulphate in the extracted material, the calculated percent of aluminum sulphate and potassium sulphate on the original sample and from these the possible percentage of alum of the formula $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$. The factors used in this last calculation are derived below. From these factors the ratio of potash and alumina in pure alum is obtain-

ed. The ratio of extracted potash to extracted alumina is then calculated for each run and whichever is present in a minority ratio to the proper proportion for alum is used as a basis for calculating the possible yield of alum. The percent of total potash extracted is also calculated to be as shown.

$$\frac{24H_2O \cdot K_2SO_4 \cdot Al_2(SO_4)_3}{K_2SO_4} = \frac{948}{174} = 5.45$$

$$\frac{24H_2O \cdot K_2SO_4 \cdot Al_2(SO_4)_3}{Al_2(SO_4)_3} = \frac{948}{342.4} = 2.77$$

Curves were plotted for the runs at six-hundred, seven hundred, and eight hundred degrees centigrade.

RUN #1.

It was intended to start at the lower temperature range at 400° C. In beginning the work it was considered advisable to use the gas muffle. The sample of alunite used was a small one which Prof. McCormack had. A larger sample of alunite had been sent for, but had not arrived so that this sample of alunite

was used in the belief that the analysis of it would be nearly the same as that of the larger sample to come. It was soon found that the temperature of the gas muffle could not be kept constant below 900° C. so that instead of making this run at 400° C., it was made at 900° C. At the end of the second hour the sample was found to differ in no way from the first hour, showing that complete reaction had taken place during the first hour at 900° C. This temperature gave a complete extraction of the potassium without any alumina.

It was after this run that it was decided to use the electric muffle.

Data.

Wt. of ore.	temp. of roasting.	time of roasting.	percent loss in wt.
25 gr.	900° C.	1 hour.	28.5 %
25 gr.	900° C.	2 hours.	28.5 %

Percent extracted material.	calculated % $Al_2(SO_4)_3$ in extracted material.	% K_2SO_4 in extracted material.
21.5 %	0 %	100 %
21.5 %	0 %	100 %

RUN #2.

By this time the sample of alunite had arrived and was treated as described. Analysis of this was made and found to be as follows:

SiO_2 - - .68 %
Al_2O_3 - -41.83 %
K_2O - - -10.89 %

No trace of iron or manganese was found on the size samples weighed. From analysis of alunite from various parts of the world, given by various authorities, it was believed that a very small percentage, if any, sodium was present and for this reason it was not attempted to separate the alkalies.

This run was made at 400° C., the time range being up to four hours. The loss in weight and the extracted matter on all four of these samples was found to be insignificant. The exact figures are shown on the data sheet.

Data. (Run #2)

Wt. of ore.	Temp. of roasting.	Time of roasting.	% loss in wt.	% extracted.
25 gr.	400°C.	1 hour.	0 %	0 %
25 gr.	400°C.	2 hours.	0 %	trace.
25 gr.	400°C.	3 hours.	0 %	trace.
25 gr.	400°C.	4 hours.	0 %	trace.

Calculated % $Al_2(SO_4)_3$ in extracted mat.	% K_2SO_4 in extracted material.	Possible % alum yield.	% total potash recovered.
none	none	——	——
trace	none	——	——
trace	none	——	——
trace	none	——	——

RUN #3.

This run was made at 500°C. with a time range of four hours. The results of this run were also negligible.

Data.

Wt. of ore.	Temp. of roasting.	Time of roasting.	Percent loss in wt.
25 gr.	500° C.	1 hour	1.4 %
25 gr.	500° C.	2 hours.	2.1 %
25 gr.	500° C.	3 hours.	4.3 %
25 gr.	500° C.	4 hours.	4.6 %

% extracted material	Calculated % $Al_2(SO_4)_3$ in extracted mat.	% K_2SO_4 in extracted material.
.2 %	trace	63 %
.32%	trace	65 %
.6 %	trace	66.6 %
.8 %	trace	98 %

Data. (Run #3 cont'd.)

Percent alum possible.	Percent of total K_2SO_4 extracted.

RUN #4.

A fourth run was made at 600°C. and with a time range of fours and at this temperature the first significant quantitative results were noticed.

In the previous runs the method of extraction had been to keep the roasted material in 200 cc's of water at about 90° C. for several hours. In using this method it was found that the alunite set and formed a hard cake in the bottom of the vessel. On this run it was decided to attempt to overcome this difficulty by a more rapid leaching with water. The roasted material was covered with about 150 cc's of water which was kept at about 90° C

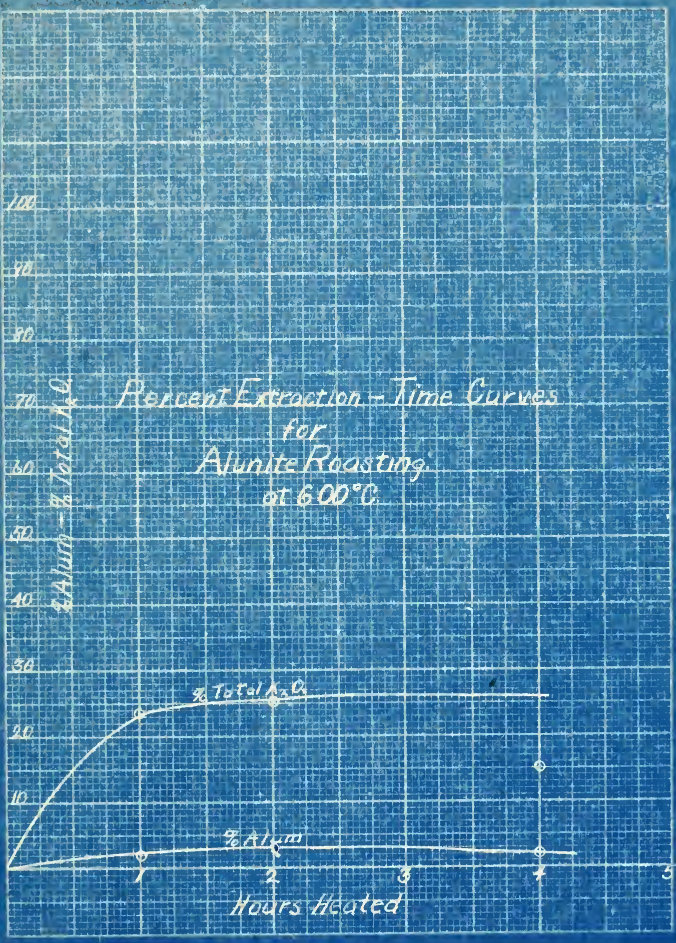
and the whole mass was constantly stirred for about ten minutes. It was then allowed to settle and was filtered. The residue was again treated with warm water as before and again filtered. The two filtrates were combined. In this way the setting of the alunite into the hard rock-like mass was prevented and, as can be seen from the data sheet, the extraction was fairly efficient.

Data.

Wt. of ore.	Temp. of roasting.	Time of roasting.	% loss in wt.
25 gr.	600° C.	1 hour	13.6 %
25 gr.	600° C.	2 hours.	14.0 %
25 gr.	600° C.	3 hours.	14.8 %
25 gr.	600° C.	4 hours.	15.20%

% of extracted material.	Calculated % $Al_2(SO_4)_3$ in extracted mat.	% K_2SO_4 in extracted material.
37.72 %	2.27 %	12.72 %
5.57 %	16.74 %	81.2 %
6.00 %	19.8 %.	59.4 %
3.74 %	23.38 %	72.8 %

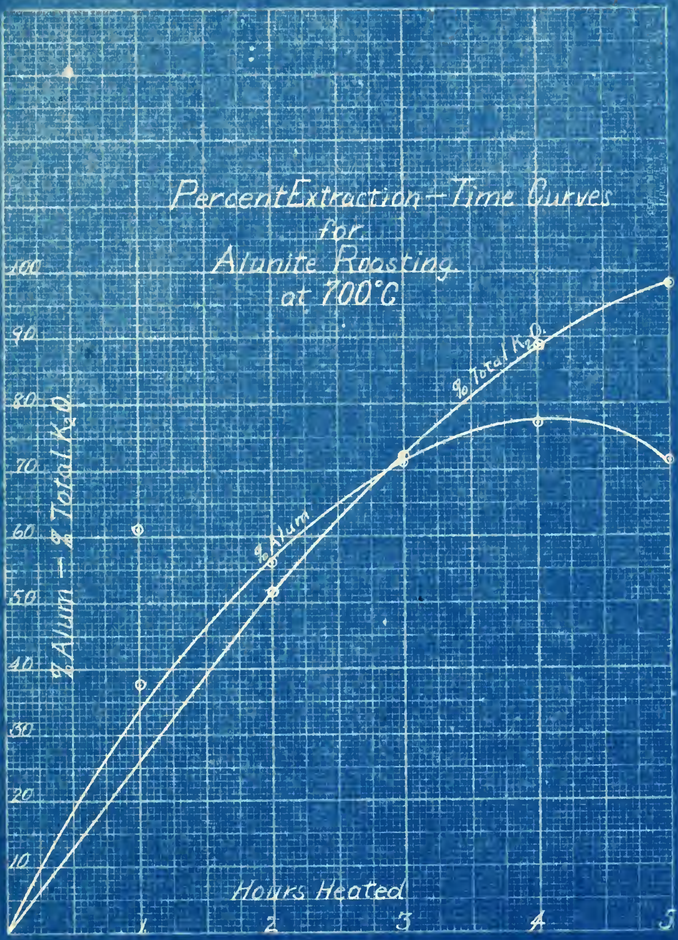
Percent Alum possible.	Percent total K_2SO_4 extracted.
2.34 %	23.9 %
2.58 %	22.5 %
2.47 %	17.7 %
2.42 %	13.5 %


Percent Extraction - Time Curves
for
Alunite Roasting
at 600°C
% Alum - % Total K₂O
100
90
80
70
60
50
40
30
20
10
% Total K₂O
% Alum
1
2
3
4
5
Hours Heated

F-M.M.W.

RUN #5.

This run was conducted with the time range of four hours and temperature at 700° C. It was becoming apparent that the percentage of matter extracted was, so far, increasing with the time and temperature. At the second hour of this run it was noticed that visible fumes and sulphur trioxide were coming off. This seemed to point to the fact that the maximum point was being reached since any great decrease in the sulphate radical would merely mean a decrease in the amount of soluble alumina. The limit of four hours on this run, however, showed no decline in the percentage of extracted matter. As had been the case so far, the fourth hour run at 700° C, being the longest time at the highest temperature.(with exception of the 900° run). showed the greatest percentage of extracted matter so far obtained


Percent Extraction – Time Curves
for
Alunite Roasting
at 700°C
100
90
80
70
60
50
40
30
20
10
% Alum – % Total K₂O
% Alum
% Total K₂O
Hours Heated
1
2
3
4
5

MMW.

Data for Run #5.

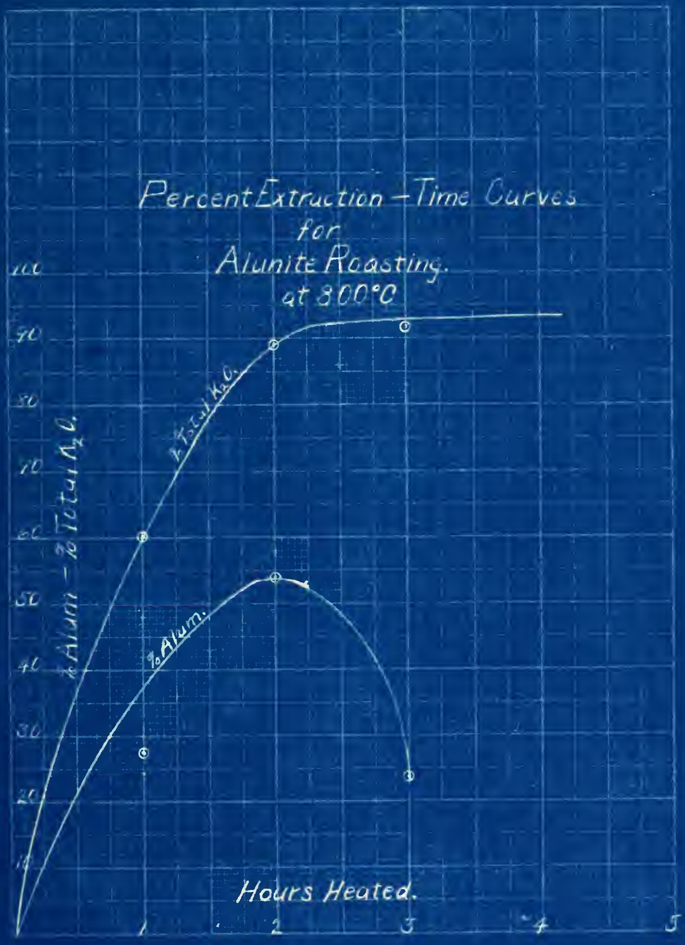
Wt. of ore.	Temp. of roasting.	Time of roasting.	% loss in wt.	% of extracted material.
25 gr.	700° C.	1 hour.	16.40 %	48.68 %
25 gr.	700° C.	2 hours.	17.88 %	41.12 %
25 gr.	700° C.	3 hours.	21.36 %	52.00 %
25 gr.	700° C.	4 hours.	18.40 %	48.80 %
25 gr.	700° C.	5 hours.	22.24 %	52.04 %
25 gr.	700° C.	6 hours.	26.20 %	39.57 %

Calculated % $Al_2(SO_4)_3$ in extracted material.	% K_2SO_4 in extracted material.	% Alum possible.	% total K_2SO_4 extracted.
27.80 %.	25.44 %	37.48 %	61.5 %
53.92 %	25.08 %	56.19 %	51.4 %
49.58 %	27.72.%	71.31 %	71.7 %
57.20 %	36.72 %	77.30 %	89.0 %
49.70 %	37.90 %	71.63 %	98.0 %
2.48 %	50.40 %	27.17 %	98.9 %

RUN #6.

This run, in accordance with the previous runs, was made at 800° C. The percentage of extracted matter on this run was showing a steady decrease below the fifth run with each increase of time so that the run was stopped at the end of the third hour.

The data so far obtained, had showed the


Percent Extraction – Time Curves
for
Alunite Roasting.
at 800°C
100
90
80
70
60
50
40
30
20
10
% Alum – % Total K2O.
% Total K2O.
% Alum.
Hours Heated.
1
2
3
4
5

M.M.W.

temperature at 700° C to be the best temperature at which to work. However, this run had not been carried beyond a maximum point in the yield so that it was impossible to state whether the maximum point had been reached or not. For this reason one more run was made.

Data.

Wt. of ore.	Temp. of roasting.	Time of roasting.	% loss in wt.	% of extracted material
25 gr.	800° C.	1 hour.	14.92%	29.84 %
25 gr.	800° C.	2 hours.	24.60%	43.44 %
25 gr.	800° C.	3 hours.	32.76%	27.12 %

Calculated % $Al_2(SO_4)_3$ in extracted material.	% K_2SO_4 in extracted material	% Alum possible.	% of extracted material.
29.48 %	30.84 %	24.34 %	45.7 %
45.00 %	41.18 %	54.15 %	89.0 %
31.48 %	66.90 %	23.62 %	90.3 %

RUN #7

This run was made to follow run #5. The temperature was kept at 700°C. and two samples were run, one for five hours, the other for six hours. Upon carrying these samples through

the usual routine, it was shown definitely that the maximum point was at four hours and at 700° C.

The fifth run had shown the best conditions under which to operate and it was now decided to try out these conditions on a somewhat larger scale and use operating conditions somewhat similar to those which would be used industrially. One hundred forty two grams of the material were roasted under the best conditions, followed by leaching with water and this in turn followed by evaporation and crystallization of the alumina. Upon evaporation the solution showed fairly large weights of precipitate which was filtered off and could not again be put into solution. Upon concentration and crystallization, three crops of crystals giving a total yield of 60 % of alum, was obtained. In calculating the ratios of potash and alumina given experimentally by the best conditions, it was seen that

the yield of alum should have been above 75%. Upon considering the matter, it was decided that this yield was not obtained on the larger run due to an insufficient amount of the sulphate radicle. The material which went into solution was evidently the basic alum described by Blount and Bloxam. An equally large scale run was made on 200 grams of the ore, treated in a similar manner to the previous run with the exception that before concentrating the solution for crystalization, enough sulphuric acid was added so that solution gave an acid reaction to litmus. This was a small amount in this case, being about one cubic centimeter. This liquid gave a yield of 75% of alum crystals in two crops. The remaining liquid was discarded.

CONCLUSION.

It is evident that the best conditions for the extraction of all alum from the sample of alunite used are a roasting at 700° C. for four hours followed by a repeated leaching. After filtering, the filtrates are concentrated by one means or another and the alum allowed to crystallize.

Time was not available for the investigation of samples of alunite of any other composition than this one so that it is impossible to state whether these conditions will hold for all alunite samples or not. That alunite from various parts of the world varies in composition is evident from the analysis given by various authorities. This difference in composition may account for the varied conditions for treatment given.

This work was done, as stated, in the electric muffle. It would probably be advisable, before using any such process as this on a large scale, to make a few short investi-

gations as to the results obtained by roasting with the heat of an open flame such as would be the condition in a lime kiln or reverberatory type of oven.

It was observed that after roasting the rock in small pieces, the pieces were very friable at the end of the operation. In the industrial operation of such a process as this, it would probably be advisable to roast the material in small lumps which could then be easily pulverized in a roll mill. The pulverized material would give more efficient leaching than the lumps. The leaching should be carried out by warm water in some form of tank fitted with a stirring device to keep the material in agitation while leaching. This vat should be arranged with some sort of conical bottom so as to render the removal of the residue alunite easy. As the leaching liquor settles out very clear, a small filter press would handle a large volume of the liquor to

remove all remaining undissolved solid matter. Wooden or lead lined tanks could be used for the concentration and crystallization of the material. Such vats could be heated by steam coils. A vacuum evaporator could probably be used efficiently for concentrating the liquor before crystallizing. After recovery the alum crystals could be dried in air.

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